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THE DOW CHEMICAL COMPANY

MIDLAND MICHIGAN

ANALYTICAL LABORATORIES

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REPORT

APR 27 1983

DATE June 4, 1971

CHARGE

AL NUMBER (continued)

PROBLEM

YOUR NUMBER Sample Nos. 333-2-102-1, -2, -3

DESCRIPTION PARTITION COEFFICIENTS OF BIPHENYL, DIPHENYL OXIDE AND DOWTHERM® A BETWEEN 1-OCTANOL AND WATER -- ANOTHER LOOK

SUMMARY

It was called to our attention that the partition coefficients which we had previously reported for biphenyl and diphenyl oxide (4-20-71) were widely at variance with values reported by others (1-5). Therefore, the determination was repeated on the same samples, using an improved method designed to eliminate the major possible sources of error in our earlier work. This method is believed to be equal or superior to some published procedures. However, our experience indicates that for a compound with a partition coefficient greater than 10,000, the coefficient determined by ultraviolet spectrophotometry may be of dubious accuracy. Details of the procedure are given in the Experimental section. The results tabulated below for biphenyl and diphenyl oxide do not correspond to literature values, and are not independent of concentration in octanol.

RESULTS

Sample No.	Sample Name	Partition Coefficient Octanol/Water	Initial conc. in Octanol, mg/ml
333-2-102-1	Biphenyl (a)	186,000	20
333-2-102-1	Biphenyl	287,000	10
333-2-102-2	Diphenyl oxide (b)	58,000	20
333-2-102-2	Diphenyl oxide	67,000	10
333-2-102-3	Dowtherm® A	28,000	20
333-2-102-3	Dowtherm® A	20,000	10

Literature Values: (a) 12,300 (8); 1445 (4). (b) 16,220 (8)

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EXPERIMENTAL

In order to avoid errors due to changes in volume or solvent composition of the phases, each solvent was initially saturated with the other solvent before any solutions were prepared. 1-Octanol (Eastman No. 871) saturated with water was used for preparation of standard solutions in octanol, partitioning runs, dilutions, and reference solvent. Distilled water saturated with 1-octanol was used for preparation of aqueous standard solutions, partitioning runs, and reference solvent when reading water solutions.

To eliminate error from possible absorption of sample compound on the walls or cap liner of the partitioning bottle, the concentration of sample in each phase was determined independently, using separate standardization values derived for each solvent. See Table 1.

The concentration of sample in the water phase after partitioning must be below its solubility limit. Comparison of our highest measured concentrations of biphenyl and diphenyl oxide with reported (6, 7) maximum solubilities of 7.5 and 20.8 ppm respectively, showed that we were far below the limits. Also, aqueous standard solutions at two different levels, with at least one above any concentration found, yielded similar absorptivities.

The procedure used was as follows: A solution of the sample in octanol was prepared, either directly or by dilution from a more concentrated solution, in the bottle to be used for partitioning. An equal volume of water was added, the bottle was tightly capped with a "Polyseal" cap, and shaken for 3 hours on an Eberbach reciprocating tray shaker operating at 170 cycles per minute. The bottle size was chosen to avoid excessive air space but allow good mixing of the phases. Bottles were shaken lengthwise on their sides, then placed upright for a phase separation period of 16 hours to 2 days. The clear octanol layer was always sampled first, using microliter syringes to give one-step dilutions suitable for ultraviolet absorption study in 1-cm cells. The water layer (always slightly hazy even after 2 days) was carefully withdrawn by volumetric pipet and centrifuged to clarify it, then examined undiluted in 5-cm and 10-cm cells by ultraviolet spectrophotometry. The concentration of sample in each layer was calculated from the applicable absorptivity value, which was an average from the two highest standard concentrations.

In the first set of partitioning runs, each sample was tested at three concentrations in octanol: 2, 1 and 0.4 mg/ml. The water layers showed no detectable levels of the compounds, not even for the more sensitive biphenyl in 10-cm cells. Another set was run at 10 and 20 mg/ml in octanol, and this time measurable amounts of material showed up in the water layers. However, as the spectra in Figure 1 indicate, there may be something else in addition to the expected compounds. Results are summarized in Table 2.

CALCULATIONS

1. absorptivity = a = $\frac{A}{bc}$ = $\frac{\text{absorbance}}{\text{light path, cm x conc. in g/l or mg/ml}}$

2. concentration, mg/ml = $\frac{\text{A x dilution factor}}{\text{absorptivity x cell length, cm}}$

3. Partition coefficient = $\frac{\text{concentration in octanol}}{\text{concentration in water}}$

The wavelengths and absorptivities actually used to calculate the concentrations reported in Table 2 were as follows (P = peak, Sh = shoulder, SP = shoulder peak):

	In Octanol		In Water	
Sample	nm	a	nm	a
Biphenyl	249 P	111	248 P	110
Diphenyl oxide	225 Sh	60.3	268 P	9
Dowtherm® A	234 SP	54.5	234 Sh	43.5

REFERENCES

1. C. Hansch, et al., J. Am. Chem. Soc. 85, 2817 (1963).
2. C. Hansch and T. Fujita, J. Am. Chem. Soc. 86, 1616 (1964).
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4. K. Rogers and A. Cammarata, J. Med. Chem. 12, 692 (1969).
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7.
8. C. Church, "unpublished analysis".

Table 1. Standardizations for Ultraviolet Analysis

Sample	In Water-saturated Octanol				In Octanol-saturated Water			
	µg/ml	nm	A1-cm	a	µg/ml	nm	A5-cm	a
Biphenyl	10.00	249	1.115	111.5	0.478	248	0.260	109
Biphenyl	5.00	249	0.553	110.6	0.191	248	0.106	111
Biphenyl	2.00	249	0.221	110.5	--	--	--	--
Diphenyl oxide	10.00	225	0.596	59.6	0.394	225	0.106	54
Diphenyl oxide	5.00	225	0.305	61.0	0.158	225	0.041	52
Diphenyl oxide	2.00	225	0.124	62.0	0.384	268	0.018	9
Dowtherm® A	10.00	234	0.543	54.3	1.012	234	0.225	44.5
Dowtherm® A	5.00	234	0.273	54.6	0.405	234	0.086	42.5
Dowtherm® A	2.00	234	0.107	53.5	--	--	--	--

Table 2. Summary of Partitioning Experiments

Sample	Initial mg/ml in Octanol	Final Conc., mg/ml		Partition Coefficient* Octanol/Water
		Octanol	Water	
Biphenyl	20.00	20.09	0.000108	186,000
Biphenyl	10.00	10.05	0.000035	287,000
Biphenyl	2.00	2.01	Not detected	--
Biphenyl	1.00	1.01	Not detected	--
Biphenyl	0.40	0.405	Not detected	--
Diphenyl oxide	20.00	19.70	0.00034	58,000
Diphenyl oxide	10.00	10.02	0.00015	67,000
Diphenyl oxide	2.00	1.90	Not detected	
Diphenyl oxide	1.00	0.98	Not detected	
Diphenyl oxide	0.40	0.40	Not detected	
Dowtherm® A	20.00	19.80	0.00071	28,000
Dowtherm® A	10.00	10.07	0.00050	20,000
Dowtherm® A	2.00	2.00	Not detected	--
Dowtherm® A	1.00	1.00	Not detected	--
Dowtherm® A	0.40	0.40	Not detected	--

* Values rounded to nearest thousand

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MIDLAND, MICHIGAN | ANALYTICAL LABORATORIES | August 12, 1971

D. C. Kaufman

PARTITION COEFFICIENTS OF BIPHENYL AND NAPHTHALENE BETWEEN 1-OCTANOL AND WATER

Wide discrepancy between the log P values for biphenyl reported by Hansch and those by Garner (AL 25-731) have been shown to be caused by volatilization of biphenyl from the separated aqueous layer before analysis by the latter chemist.

Analysis by a corrected technique gave log P for biphenyl = 4.17 ±0.03, corroborating Hansch (4.10), and log P for naphthalene = 3.59 ±0.05.

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PARTITION COEFFICIENTS OF BIPHENYL AND NAPHTHALENE BETWEEN 1-OCTANOL AND WATER

EXPERIMENTAL

Reagents

The biphenyl used was Eastman ACS grade 99.8% pure by differential scanning calorimetry; the naphthalene was crystallized 3 times from 95% ethanol, MP 79.6-80.1°C. The octanol used was Eastman #871 saturated with water. The water used was saturated with octanol. The methanol was Burdick and Jackson distilled grade.

Apparatus

International Centrifuge model SBV equipped with a multispeed attachment capable of operation up to 20,000 rpm. Cary recording spectrophotometer model 14.

Procedure

Solutions of the sample in octanol were prepared by accurately weighing the samples into 25-ml volumetric flasks and making to volume with octanol; the solutions had concentrations of 20.00 and 30.00 mg/ml.

Partitioning was done by adding 200 ml of water and 20.0 ml of sample solution to 8-oz. french square narrow-mouth bottles which were previously cleaned and dried. The bottles were closed with polyseal caps and shaken from 4-6 hours on a Eberbach reciprocating tray shaker operating at about 150 cycles per minute. Bottles were shaken lengthwise on their sides, then placed upright for 2 to 10 days to allow the phases to separate.

The clear octanol layer was carefully removed by means of pipet and medicine dropper and transferred to a small bottle for subsequent analysis. The analysis of the organic layer was performed by removing a 20- to 50-µl aliquot using a 50-µl syringe and transferring the aliquot to a 100-ml volumetric flask. The flask was made to volume with methanol and the absorbance of the solution determined at the absorption peak in 1-cm quartz cells. Standard solutions were prepared in the same manner using the same syringe and the unpartitioned portion of the octanol sample solution. The absorptivity of the standard biphenyl in octanol solution was 111 ml/mg/cm. at 247 nm. The value for the standard naphthalene in octanol was 43.2 ± .3 at 274 nm.

Aliquots of the cloudy aqueous layer were carefully removed by means of a volumetric pipet. The tip of the pipet was covered with wet cotton to repel any of the octanol layer which may still be present. The aliquots were then centrifuged for various times. Glass tubes were used at 1500 rpm and stainless steel tubes at 10,000 rpm. The centrifuged liquid was then carefully transferred to a 1, 2.5 or 5-cn. cell and the absorbance recorded from 230 to 350 nm. The concentration of sample in the water was then determined from its absorption peak at 248 or 276 nm. Standard solutions of sample in water were prepared by dissolving an accurately weighed (microbalance) portion of sample in 25 ml of methanol followed by dilution to one liter volume in water. The absorptivity of the standard biphenyl in water was 107 ±1 ml/mg/cm at 248 nm (average of three trials); the value for naphthalene in water was 36.6 at 276 nm (one trial).

The partition coefficients were calculated in the usual manner. The concentration of sample in the organic layer was divided by the concentration of sample in the aqueous layer. The results are summarized in Table 1. The organic layer analyzed the same before and after the partitioning (30.0 and 40.0 mg/ml).

DISCUSSION

The aqueous layer was centrifuged in the absence of the organic layer except for the four trials listed in the table. Apparently a loss of sample does occur under these conditions despite the fact that the concentration of sample in the water is well below the solubility concentration. The experimental plan was to centrifuge for 15-minute intervals until the concentration leveled off at a constant value. As can be seen from the table, this result was never achieved and it appears that the concentration would eventually reach 0 if the solutions were centrifuged long enough. In every case the centrifuged solutions were crystal clear, or at worst, very slightly hazy to the eye. From the results listed in Table 1 it appears that the previously reported work of Garner (1) is in error, his high values being obtained by volatilization of biphenyl from the water layer. The value from the present work (based on analyses of aqueous layer at earliest clarification) corroborate the Hansch data.

cpd.	log P found	log P literature
Biphenyl	4.17 ±0.03	4.10 (2)
Naphthalene	3.59 ±0.05	3.37 (4)

Table 1

Sample	Initial Conc. Octanol Layer mg/ml	Treatment of Aqueous Layer	log P
Biphenyl	30.0	filtered, not centrifuged (hazy)	4.044
Biphenyl	30.0	15 min. at 1500 rpm (clear)	4.204*
Biphenyl	30.0	30 min. at 1500 rpm (clear)	4.262
Biphenyl	30.0	45 min. at 1500 rpm (clear)	4.543
Biphenyl	30.0	5 min. at 10,000 rpm (clear)	4.237
Biphenyl	30.0	10 min. at 10,000 rpm (clear)	4.319
Biphenyl	30.0	15 min. at 10,000 rpm (clear	4.413
Biphenyl	30.0	10 min. at 10,000 rpm with organic layer	4.157*
Biphenyl	40.0	filtered, not centrifuged (hazy)	4.052
Biphenyl	40.0	15 min. at 1500 rpm (clear)	4.150*
Biphenyl	40.0	30 min. at 1500 rpm (clear)	4.242
Biphenyl	40.0	45 min. at 1500 rpm (clear)	4.352
Biphenyl	40.0	5 min. at 10,000 rpm (clear)	4.256
Biphenyl	40.0	10 min. at 10,000 rpm (clear)	4.387
Biphenyl	40.0	15 min. at 10,000 rpm (clear)	4.485
Biphenyl	40.0	10 min. at 10,000 rpm with organic layer	4.171*
Biphenyl	40.0	45. min. sample after standing 5 days	5.377
Naphthalene	30.0	5 min. at 10,000 rpm (clear)	3.578*
Naphthalene	30.0	10 min. at 10,000 rpm (clear)	3.714
Naphthalene	30.0	15 min. at 10,000 rpm (clear)	3.888
Naphthalene	30.0	10 min. at 10,000 rpm with organic layer	3.565*
Naphthalene	40.0	5 min. at 10,000 rpm (clear)	3.637*
Naphthalene	40.0	10 min. at 10,000 rpm (clear)	3.731
Naphthalene	40.0	15 min. at 10,000 rpm (clear)	3.940
Naphthalene	40.0	10 min. at 10,000 rpm with organic layer	3.591*

* Values averaged to obtain reported log P.

August 12, 1971 -4-

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1.

2. Hansch, C., average of 6 determinations from letter to N^ely, June 10, 1971.

3.

4. Hansch, C., and Fagita, T., J. Am. Chem. Soc. 66, 1616 (1964).

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AN ANALYSIS OF THE DISTRIBUTION PATTERN OF
DOWTHERM® A IN A RIVER ENVIRONMENT

There are many instances where a slow leak of a chemical from a point source enters a flowing stream. One of the questions that naturally arises is concerned with the ultimate fate and distribution of the chemical in such an environment. This type of situation occurred in discussing the potential environmental impact of DOWTHERM A. From a previous report[1] it was determined that a leak of this heat exchange fluid of one pound/hour may exist at a typical plant site. Assuming all of the material enters the river we wanted to know how this material distributes and dissipates in a river system.

As the chemical flows down the stream there are three main dissipating and degradative mechanisms which are operating.

1. Volatility, i.e. loss to the air.
2. Soil absorption and metabolism by the microorganisms present in the soil.
3. Binding and metabolism by aquatic species present in the water.

These mechanisms will all tend to clear the stream of the pollutant. The hazard of the chemical to the environment will then be governed by a number of other factors such as:

1. Toxicity to marine life or life associated with an aquatic environment.
2. Rates of dissipating reactions.
3. Chemical and physical properties.
4. Level of chemical that reaches the stream.
5. The flow characteristics of the stream in question.

It is the purpose of this report 1. to propose a mathematical model for integrating the dissipating mechanisms and 2. to

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generate data on DOWTHERM A and fit it to the model in order to arrive at the concentration profile of the chemical in a typical river.

The Model

Consider a small section of river as shown in Figure 1, where the chemical coming in is represented by $C_{(x)}$ (lbs/lb H_2O) and the chemical leaving is $C_{(x+dx)}$. The material balance on this small section is given by Equation 1.

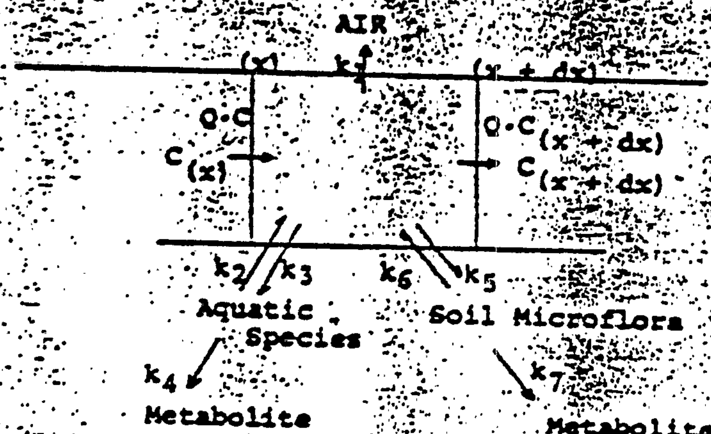


Figure 1

$$-Q \frac{dc}{dx} dx = \Sigma \text{ dissipating reactions} \quad (1)$$

where Q is lbs of water/hour in the stream moving through section dx.

The rate equations for the three types of dissipating reactions are described below.

AIR

Rate of loss in lbs/hour from a river surface is given by Equation 2.

rate of loss (lbs/hour) = $k_1 C_{(x)} W \cdot dx$ (2)

where w is width of river in feet.

k_1 is in units of lbs/hour/sq. ft.

AQUATIC SPECIES

To a first approximation the rate of loss *via* metabolism by aquatic species is given by Equation 3.

$$C + F \underset{k_3}{\overset{k_2}{\rightleftharpoons}} CF \xrightarrow{k_4} \text{Products} \quad (3)$$

Where C = chemical

F = aquatic species (lbs/sq.ft. of water).

Rate of loss in forward reaction is given by Equation 4.

$$(\text{lbs/hr}) = k_2[C][F]w \cdot dx \quad (4)$$

where k_2 is hr^{-1}

w is width in feet

F conc. of aquatic species in lbs/sq. ft.

Rate of back reaction is given by Equation 5.

$$(\text{lbs/hr}) = k_3[CF]w \cdot dx \quad (5)$$

The assumption is made that $k_2 >> k_4$ consequently at equilibrium we have 6.

$$[CF] = \frac{k_2}{k_3}[C][F] \quad (6)$$

Finally the rate of loss in lbs/hour *via* metabolism is shown by Equation 7.

$$\text{Rate of loss (lbs/hour)} = k_4 \left(\frac{k_2}{k_3}\right) C.F.w.dx \quad (7)$$

SOIL

In a similar manner to the above we can arrive at Equation 8 which represents the loss *via* soil absorption and metabolism.

$$\text{Rate of loss (lbs/hr)} = k_1(\frac{k_5}{k_6})C.S.L.dx \quad (8)$$

This equation assumes absorption to the soil microflora with subsequent metabolism where L = contour width of the stream bottom in feet and S is the weight of soil in lbs/sq. ft.

Equating Equation 1 with 2, 7, and 8 yields Equation 9.

$$-Q\frac{dc}{dx}dx = k_1Cw.dx + k_4(k_2/k_3)C.F.w.dx + k_7(k_5/k_6)C.S.L.dx \quad (9)$$

Rearranging 9 yields 10.

$$\frac{dc}{dx} = -\frac{C}{Q}[k_1w + k_4(k_2/k_3)F.w + k_7(k_5/k_6)S.L] \quad (10)$$

This can now be integrated to yield 11.

$$C = C_oe^{-Kx} \quad (11)$$

Where K = the quantity in square brackets in 10 divided by C.

Equation 11 is a simplified scheme to describe the concentration profile of a chemical C as it moves down a river subjected to the various dissipating mechanisms mentioned previously. It must be recognized that since this is a very elementary model of necessity it contains a number of assumptions.

1. Rates of metabolism are slow compared to absorption and desorption phenomena.

2. There is a constant flow of water in the stream of a constant width. Normally the flow of water will increase as you go downstream due to the increased number of tributaries. Such increased flow will also result in increased width.

3. The composition of a river bottom and aquatic species is both uniform and constant.

4. It is assumed that the surface of the river is unagitated, hence evaporation is taking place from an unbroken uniform surface.

Accepting these assumptions will normally lead to a higher concentration of calculated chemical than would actually be present. Consequently the model as presented has a number of built in safety features.

In the next section the parameters needed to satisfy Equation 11 will be derived using DOWTHERM A as the chemical and the Tittabawassee River as the stream.

EXPERIMENTAL DATA

AIR

The proposed model for analyzing the rates of dissipation of a chemical from a river requires a valid rate constant to measure the exit *via* volatility. In considering this avenue of exit further a material balance equation (12) may be set up for a small section *dx* of the river.

$$Q\frac{dc}{dx}dx = -kC_{(x)}w\cdot dx \qquad (12)$$

Where k is given in units of lbs/hr/sq.ft.
Q is lbs water/hour

In order to measure k experimentally the following procedure was used. It was demonstrated (Figure 2) that a linear relation existed between concentration of DOWTHERM A in water and optical density at 250 mu in the range of 2-20 µg/ml of the chemical. Using this as an analytical tool the loss of chemical *via* evaporation was measured. Several evaporating dishes of different heights were arranged in the hood at ambient temperature (20°C). These were filled to the top with a DOWTHERM A

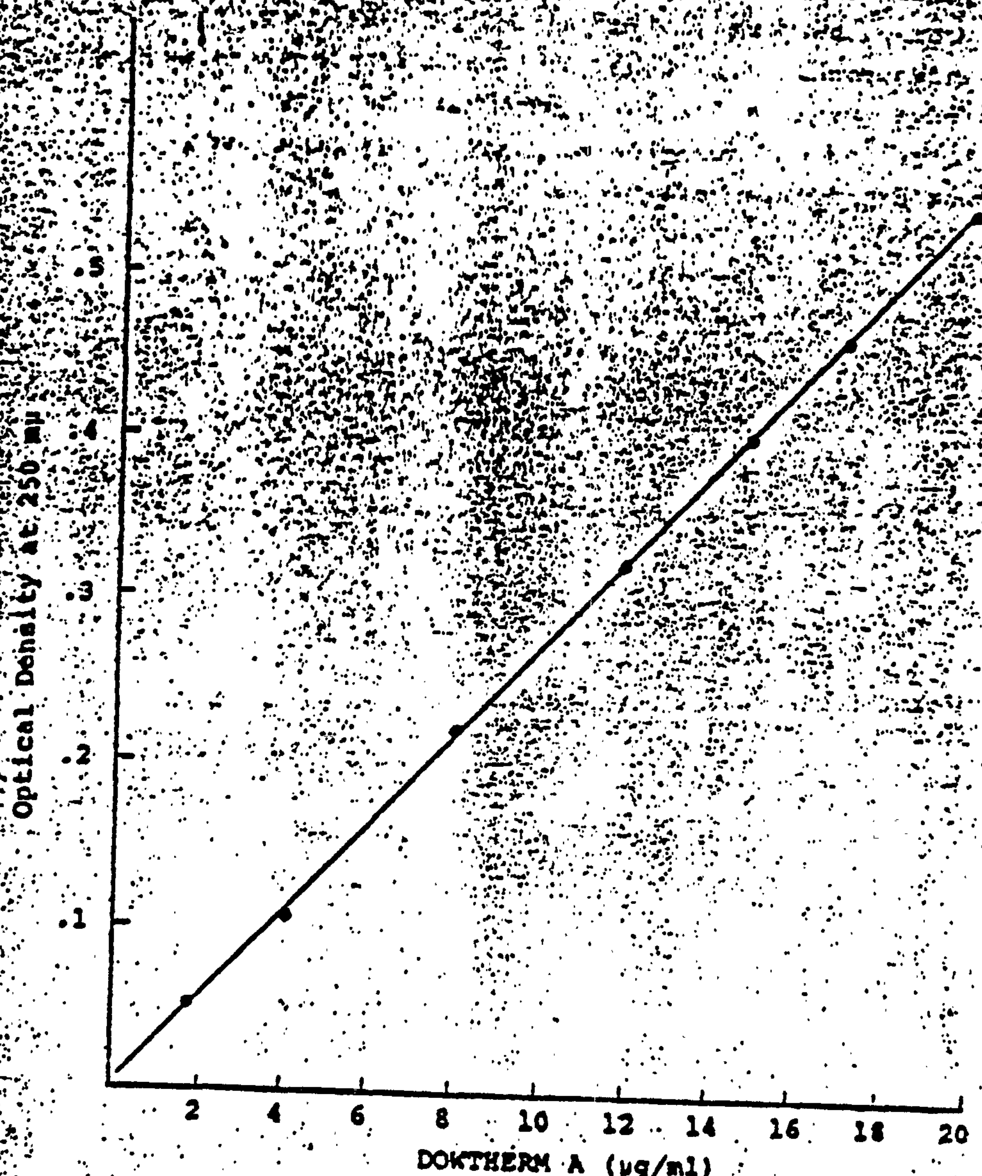


Figure 2. Standard Curve for DOWTHERM® A

solution of approximately 20 µg/ml. Control samples were stoppered; one was placed in the laboratory exposed to room light and another one was placed in the dark. At zero time and at periodic intervals samples were taken and analyzed by means of optical density measurements. In addition the height of the liquid in each container was measured. The results are summarized in Table I and Figure 3.

The material balance for these containers is given by Equation 13.

$$\rho v \frac{dc}{dx} = -kA \cdot C \tag{13}$$

Where: ρ = density of water (62.5 lbs/cu.ft.)
v = volume
A = area
C = concentration

Rearranging 13 gives 14.

$$\frac{dc}{dt} = \frac{-KA \cdot C}{\rho v} \tag{14}$$

which on integrating yields 15.

$$C(t) = C_o e^{\frac{-KA}{\rho v} \cdot t} \tag{15}$$

Since $A/v = 1/h$, therefore

$$C(t) = C_o e^{\frac{-K}{\rho h} \cdot t} \tag{16}$$

The experimental K derived from the data is equal to $k/\rho h$, therefore the k that is needed for the river equation is given by 17.

$$\therefore k = 62.5 \times h \text{ (feet)} \times K \tag{17}$$

Where $K = 1/t \ln C_o/C_t$

TABLE I

Summary of Volatility Experiments with DOWTHERM® A

Sample	h (ft)	k*
1	.292	1.135
2	.264	1.236
3	.186	1.106
4	.144	1.108
5	.106	1.152

*k in lbs/hr/sq.ft. calculated by means of the following formula $k = 62.5 \times h \times 1/t \times \ln C_o/C_t$ derived in the body of the text.

There was no loss of DOWTHERM A in the stoppered bottles either stored in the dark or under laboratory lights during the time of this experiment.

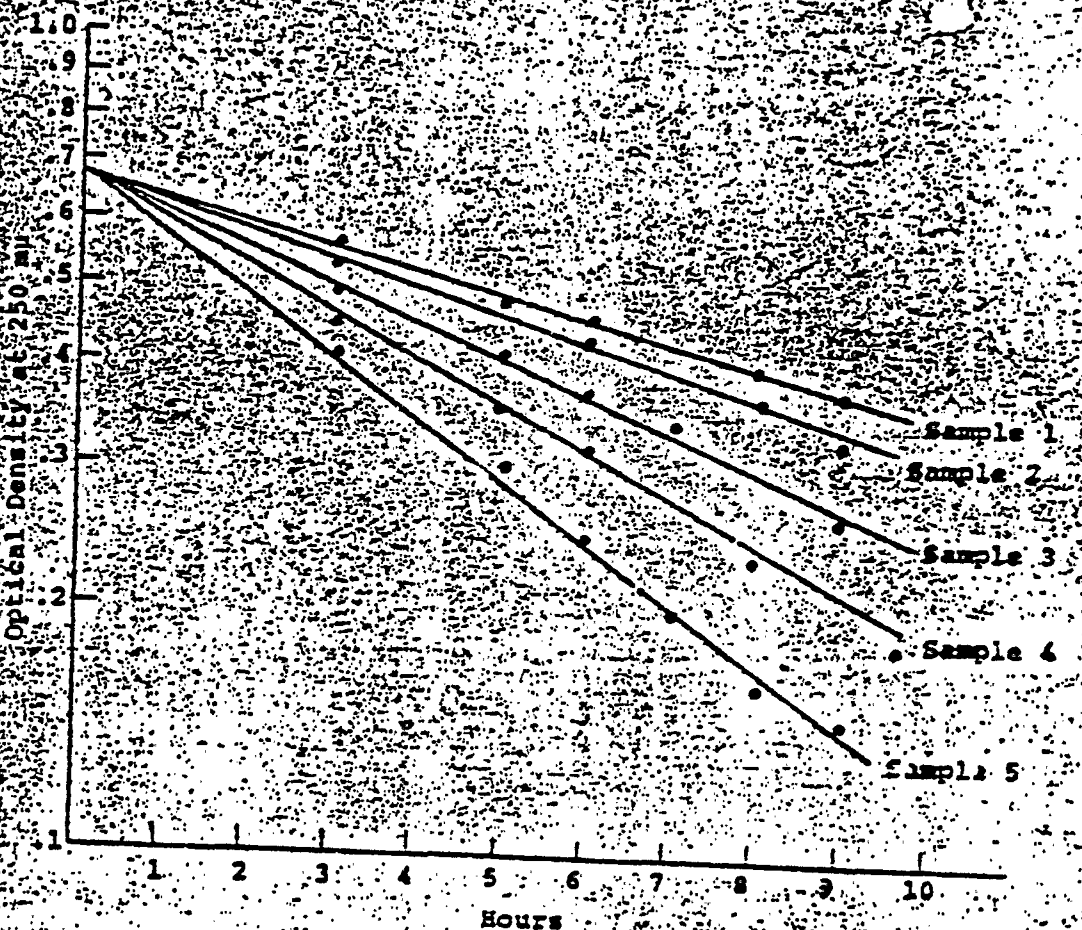


Figure 3. Volatility of DOWTHERM® A from Water.
Sample Nos. Refer to TABLE I.

The derived values for k are shown in Table I. It is this value which will be used in solving Equation 11.

SOIL

In examining equation 8 which represents the loss of chemical *via* the soil the following parameters need to be quantified.

i) k_7 the rate of metabolism
ii) k_5/k_6 soil adsorption constant
iii) S conc. of soil in lbs/sq.ft.

i) The rate of metabolism was approximated from the data reported by Knop *et al.*[2] These authors used sterilized Tittabawassee River and inoculated it with nonsterile bottom sediment containing 50 PPm DOWTHERM A. At 5 days approximately 20% of the diphenyloxide and 35% of the diphenyl was consumed. Assuming a first order reaction and assuming 30% consumption of DOWTHERM A in 5 days, a rate constant may be calculated from Equation 18.

$$k = \frac{1}{5 \times 24} \ln \frac{100}{70} \tag{18}$$

$$= .00297 \text{ hr}^{-1}$$

ii) Soil adsorption constant was calculated by Knop *et al.*[3] to be 66 for a high organic soil. Using a low organic soil we calculated a value using a procedure described by Hamaker[4] to be 2.5. Assuming that most river bottoms will contain a fairly high organic content, a value for k_5/k_6 of 30 will be used in the river equation. Another assumption is that soil absorption is similar to absorption to the microflora present in the soil.

iii) Based on figures used by the Agricultural Laboratory[5] the weight of an acre of ground 3" thick is approximately 1×10^6 lbs. This calculates out as 23 lbs/sq. ft.

AQUATIC SPECIES

This is the area where estimations are extremely difficult and very tenuous at best. In looking for units to express biomass concentration, the book by Kendeigh[6] was most useful. On page 55 he reports some average data for a mud bottom Silver Spring stream in Florida; on a dry weight basis plants averaged 809 g/m^2, herbivores 37 g/m^2, small carnivores 11 g/m^2, and large carnivores 1.5 g/m^2. The crop of fish in Indiana streams varied from 5.2 to 106 g/m^2. The fish crop in warm streams is generally higher than in cool streams. As you can see it becomes very dangerous to settle on one figure for the concentration of biomass/sq. foot of stream. However, as will be seen shortly when concentration profiles for the chemical are calculated the amount of chemical dissipated by aquatic metabolism is rather small. Consequently, the accuracy of this figure takes on less importance. To a first approximation a figure of 500 lbs biomass/acre of stream will be used (0.0115 lbs/sq.ft.).

With the realization that the aquatic biomass does not represent a main avenue of dissipation, the constants for rate of metabolism and absorption become less critical. The absorption constant was estimated as follows: From data of G.N. Smith[7] a value of 97 was obtained for absorption of DURSBAN® to fish. Since this insecticide has a partition coefficient between octanol and water of 35000[8] which is three times the value of DOWTHERM A[1] a value for k_2/k_3 of 30 will be used. Assuming a half-life of about 10 days for the metabolism and clearance of DOWTHERM A gives a value or k_4 of 3×10^{-3} hr^{-1}. It could be considerably faster.

RIVER CHARACTERISTICS

An average flow of the Tittabawassee of 1000 cubic feet/sec. and an average width of 150' and an average contour width of 160' will be used in the modeling exercise.

APPLICATION OF DATA TO RIVER MODEL

A small Basic program was written to handle Equation 11. A print-out of this program is shown in Figure 4. A few remarks are necessary to clarify the input.

1. Step 5 gives the river characteristics where w is width in feet, t is contour width, v is volume of water in cfs and A is amount of chemical added in lbs/hour.

2. Step 8 is identified as follows: H = number of data points, D = k_1, L = k_4, G = k_2/k_3, F = biomass in lbs/sq. foot, M = k_7 and J = k_5/k_6.

3. Step 16 converts v (water flow) to lbs/hour.

4. Step 35; the factors 5280 expresses the distance in miles.

Using the following data (Table II) a plot of the concentration profile of DOWTHERM A in the river may be calculated. This is shown in Figure 5.

The values for the various parameters can be varied and the influence of such variations can be seen on the calculated distance required to decrease the concentration by one half. A few variations on this half-life are shown in Table III. A few observations may be made from this exercise.

1. Loss due to biomass is insignificant compared to loss <u>via</u> soil and volatility.

2. Loss by volatility may be more important than this analysis indicates. The reason for this statement is that the above model assumes an unagitated surface which is not realistic.

TABLE II

Data to be Used in River Model

Parameter	Best Estimate
River Flow	1000 cfs
River Width	150 feet
River Contour Width	160 feet
Concentration of Chemical	1 lb/hour
Rate of Evaporation	1.1 lbs/hour/sq. foot
Soil Absorption	30
Soil Metabolism	2.97×10^{-3} hr^{-1}
Soil Density	23 lbs/sq. foot
Aquatic Absorption	30
Aquatic Metabolism	3×10^{-3} hr^{-1}
Aquatic Concentration	0.0115 lbs/sq. foot

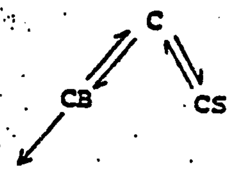
TABLE III

Influence of Parameter Changes on the Distance Required To Reduce Concentration of Pollutant by 1/2

Parameter*		Half-Distance (miles)
Control**		59.7
$k_1 = k_7 = 0$ (loss due to Aquatic Biomass)		189674
$k_1 = k_4 = 0$ (loss due to Soil)		89.8
$k_4 = k_7 = 0$ (loss due to Volatility)		178
$k_5/k_6 = 60$	Soil absorption varied	35.8
$k_5/k_6 = 90$		25.63
$k_5/k_6 = 10$		107

*All other values similar to data in Table II.
**Data from Table II.

3. Soil is a very complex media and the present model is an over simplification. For example there is at least one other competing reaction illustrated below which is important.



Where C = Conc. of chemical in water
CS = Soil chemical absorption
CB = Chemical bacteria absorption

It is the chemical bacteria absorption step which will lead to metabolism. The soil chemical complex may provide a sink for the slow continual release of chemical back into the water. A question that needs investigating is: When the chemical is adsorbed to the soil is it subject to microbial degradation?

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8. Determined by the Dow Analytical Laboratory.

Don R. Clay, Director
Office of Toxic Substances (TS-793-I)
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, DC 20460

RECEIVED JUN 29 1984

Dear Mr. Clay:

We have reviewed your letter of June 6, 1984. As a result we have reviewed the studies submitted under the 8(d) rule about which you have expressed concern.

In view of the public interest in health and safety studies subjected by your June 6 letter, we have waived claims of confidential business information in many of the studies submitted. A list of the EPA document control numbers from which CBI claims have been removed or reduced is attached. Copies of these studies have been sent separately to Tim Knutsen's attention. Studies which contain reduced claims of CBI have been re-submitted in duplicate, one copy prepared for the public files and one copy with CBI marked, as directed in the rule. In addition we have undertaken a review of our policy and procedures for asserting CBI claims in 8(d) submissions.

We appreciate your candid and informal approach to dealing with this matter, and trust that our efforts are responsive to your concern.

Very truly yours,

R. L. Hagerman
Research Associate
Regulatory and Legislative Issues
Health and Environmental Sciences
1603 Building

rt

Attachment

cc: Tim Knutson, US EPA-OTS

COMPARISON OF THE TOXICITY OF DOWTHERM* A HEAT TRANSFER FLUID AND THERMALLY DEGRADED DOWTHERM A HEAT TRANSFER FLUID TO AQUATIC ORGANISMS

March 29, 1979

D. C. Dill
Environmental Sciences Research Laboratory
Dow Chemical U.S.A.
Midland, Michigan

ABSTRACT

Fathead minnows, Pimephales promelas Rafinesque, and daphnids, Daphnia magna Straus, were exposed in static water to two different samples of DOWTHERM* A heat transfer fluid. One sample represented DOWTHERM A as sold and the other a thermally degraded DOWTHERM A (degraded by 8 weeks at 399°C in a forced circulation test unit at   Building).

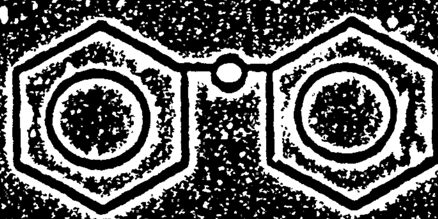
The 96-hour LC50 values for fathead minnows were 7.1 mg/L (6.3-8.0)† and 9.6 mg/L (8.3-17.6) for degraded and undegraded DOWTHERM A, respectively. The 48-hour LC50 values for daphnids were 1.27 mg/L (0.64-1.82) and 0.72 mg/L (0.26-1.05) for degraded and undegraded DOWTHERM A, respectively.

*Trademark of The Dow Chemical Company

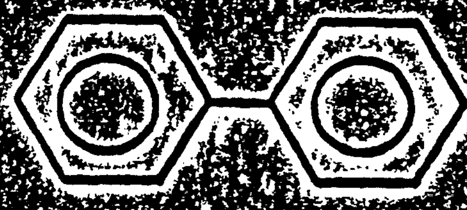
†95% Confidence ...

INTRODUCTION

DOWTHERM A heat transfer media is composed of 73.5% diphenyl oxide and 26.5% biphenyl[1]:



DIPENYL OXIDE



BIPHENYL

During the normal use of DOWTHERM A heat transfer fluid, a number of high molecular weight derivatives are formed[2]. The purpose of this study was to compare the acute toxicity of thermally degraded DOWTHERM A to fathead minnows (*Pimephales promelas* Rafinesque) and daphnids (*Daphnia magna* Straus) with that of undegraded DOWTHERM A. Simmons *et al* previously reported the 96-hour static acute toxicity of diphenyl oxide and biphenyl to fathead minnows, LC50 5.5 mg/L (4.1-7.2)* and 5.3 mg/L (4.6-6.2), respectively[3]. The solubility of these compounds in water are as follows: diphenyl oxide, 21 mg/L and biphenyl, 7.5 mg/L.

---

*95% Confidence Interval

PREPARATION OF TEST MATERIAL

The test samples of DOWTHERM A heat transfer fluid were supplied by   FP&S-TS&D, 2020 Building. The two samples came from Lot #MM06076. One represented new DOWTHERM A heat transfer fluid as sold and the other the same lot number after 8 weeks of thermal degradation at 399°F. A forced circulation test unit at 680 Building was used in preparing the degraded sample, which had the following characteristics:

1. By modified ASTM (distillation) method[4] = 10% (vol/vol) high boilers

2. GC-Flame Ionization[5]/GC-Mass Spectrometry[6]

Weight %	
85.7	DOWTHERM A
12.9	GC-Recoverable Degradation Products
1.4	GC-Unrecoverable Degradation Products[a]
100.0	

From an analysis of the mass spectral data, the following structures have been proposed for the GC-recoverable degradation products:

[a] "High boilers" which [illegible]

Isomers of this type:

biphenyl phenyl ethers + diphenoxy biphenyls + ter- and quater-phenyls	11.1%
2-phenyldiphenyl ether, triphenylmethane, benzene, phenol, dibenzofuran, 1,2-diphenylbenzene	1.8%
	112.9%

The degraded DOWTHERM A heat transfer fluid is believed to represent material from a typical customer's operation, but without contamination derived from chemicals other than DOWTHERM A.

METHODS

The static water acute toxicity tests followed the test methods described in the U.S. EPA publication, "Methods for Acute Toxicity Tests with Fish, Macroinvertebrates, and Amphibians"[7].

Fathead Minnow Toxicity Test

Fathead minnows (Pimephales promelas Rafinesque) were acclimated at 12°C to laboratory conditions for at least 10 days prior to use. They were held in a 16-hour light/8-hour dark cycle. A synthetic diet[8] was used to feed all fish during the acclimation period. Fish were not fed during the test. Test fish were placed in the bioassay vessel 24 hours prior to addition of the test compound.

Tests were conducted by placing 8 liters of carbon filtered Lake Huron water in each of 10 vessels, (8 treatment, 1 solvent control, and 1 untreated control), 22 cm deep x 24.5 cm diameter round glass aquaria, adding fish, then aerating. Stock solutions of the test compounds were prepared in acetone. The maximum amount of acetone added to any aquaria did not exceed 0.5 mL per liter of Lake Huron water. Before addition of the test compound, aeration was stopped and the test chemical added, followed by 2 liters of water for mixing, making a total volume of 10L. A refrigerated water bath maintained the temperature at 12°C ± 1°C. Ten fish were exposed to each concentration of compound. The fish were observed daily and dead fish removed.

Daphnia Toxicity Test

The acute invertebrate toxicity test consisted of exposing daphnids, Daphnia magna Straus, reared in our laboratory to various concentrations of the material in carbon filtered Lake Huron water at a temperature of 20°C ± 1°C for 48 hours, with a 16-hour light/8-hour dark cycle.

Stock solutions of the test compounds were prepared using acetone as a carrier solvent. The required amount of stock solution was combined with sufficient carbon filtered Lake Huron water to make a final volume of 200 mL in each 250 mL test beaker. A water control was set using carbon filtered Lake Huron water. Because acetone was used in the stock solutions, solvent controls were set containing the greatest amount of solvent used in any toxicant concentration. The amount of acetone was limited so that its concentration did not exceed 0.5 mL/L.

Ten first instar daphnids were added to each beaker and the beakers set in a 20°C constant temperature incubator with a 16-hour light/8-hour dark cycle. Three beakers were used for each concentration and each control. Mortality data was recorded at 24 and 48 hours. Death was defined as no response to a gentle prodding. Dead daphnids were not removed during the test.

Statistical Calculations

For each set of mortality data, the LC values and their 95% confidence intervals are given. The LC10-50-90 are the estimated concentrations of the test substance at which 10, 50, or 90% of the test organisms are dead at a specified time interval. The LC values were calculated using Finney's method of probit analyses[9] with a computer program.

RESULTS AND DISCUSSION

Two tests were run on undegraded DOWTHERM A heat transfer fluid before data was obtained which fit Finney's probit analysis program. The second test covered a narrower range of concentrations than the first. The fathead minnow LC data for degraded and undegraded, run #2, DOWTHERM A heat transfer fluid are presented in Tables I and II, respectively. The 96-hour LC50 values for fathead minnows were 7.1 mg/L (6.3-8.0) and 9.6 mg/L (9.3-17.6) for degraded and undegraded DOWTHERM A heat transfer fluid, respectively. The 96-hour LC50 values are significantly different, p = 0.05. The thermally degraded material is slightly more toxic to fathead minnows than its undegraded counterpart. Major distress symptoms noted during the test were a loss of body equilibrium (fish swimming disoriented) and melanization (darkened body color).

The daphnid toxicity tests were run three times because mortality of the control organisms exceeded 10% in the first two tests. Tables III and IV present the daphnid LC data for degraded and undegraded DOWTHERM A heat transfer fluid. The 48-hour LC values for daphnids were 1.27 mg/L (0.64-1.82) and 0.72 mg/L (0.26-1.05) for degraded and undegraded DOWTHERM heat transfer fluid, respectively. The 48-hour LC50 values are not significantly different, p = 0.05.

Dennis C. Dill 4-6-79

Dennis C. Dill
Research Biologist

APPROVED BY:

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THE DOW CHEMICAL COMPANY:

D-1033

LAB. CODE LETTERS AND REPORT NUMBER

MIDLAND, MICHIGAN

DEPARTMENT Analytical Laboratories

DATE March 29, 1974

PROBLEM NUMBER

AUTHORS I. T. Takahashi and F. A. Blanchard

TITLE Determination of Uptake and Clearance Rates of ^{14}C-Diphenyl in Rainbow Trout by Radiotracer Techniques.

INFORMATIVE SUMMARY WITH CONCLUSIONS

ABSTRACT

A radiotracer ^{14}C-diphenyl, has been used by J. S. Brosier of the Waste Control Lab and the authors to obtain bioconcentration data for diphenyl in fish. Uptake and clearance data at 1 ppb and 10 ppb exposure levels have been obtained for muscle, remainders, and whole fish in a dynamic experiment. Normalized data for whole fish at an average exposure of 1 ppb gave a clearance half-life of 64 hr and a maximum uptake after 80 hr. A bioconcentration factor of 1900 was calculated from this data.

ISSUED TO

ATTENTION OF	DEPARTMENT	ATTENTION OF	DEPARTMENT

LAB. CODE LETTERS AND REPORT NUMBER

AR100041

DETERMINATION OF UPTAKE AND CLEARANCE RATES OF ^{14}C-DIPHENYL IN RAINBOW TROUT BY RADIOTRACER TECHNIQUES

INTRODUCTION

A radiotracer study to obtain bioconcentration data for diphenyl in fish was initiated as a joint project between J. S. Brosier of Waste Control and the Analytical Laboratory in order to evaluate potential environmental problems caused by Dowtherm A (eutectic mixture of diphenyl and diphenyloxide). Previously, Dean Branson of Waste Control had completed the diphenyloxide part of the study, using ^{14}C-diphenyl oxide as a radiotracer.

Using similar radiotracer techniques, with ^{14}C-diphenyl as the radiotracer, bioconcentration data were obtained for diphenyl.

In experiments using a radiotracer, the purity and validity of the tracer plays an important part. The ^{14}C-diphenyl, Lot no. 5109:10 f-2, was synthesized by Marlene Wass of Ag-Organic Research. This tracer had a specific activity of 3.937 mCi/mmole. Since it had been stored in benzene solution for one year, its purity was redetermined by thin-layer chromatography and liquid scintillation counting by M. Wass. Two solvent systems, hexane and carbon tetrachloride, on silica gel 254F plates showed the radiopurity of diphenyl-^{14}C was 98.7%. Analytical data were also obtained on a standard sample of unlabelled diphenyl received from the Halogens Research Laboratory. Thin-layer chromatography in the same solvent systems showed only one UV detectable spot. An infra red scan by R. A. Nyquist (AL 62-213) and gas chromatographic analysis by Tom Peters showed no obvious impurities in the unlabelled diphenyl.

EXPERIMENTAL

Preparation of the Tracer

The ^{14}C-diphenyl at a sp. act. of 3.937 mCi/mmole was received in a benzene solution with a concentration of 13.708 mg/50 ml. 39.4 ml of the solution (10.80 mg diphenyl) was placed in a flask and mixed with 12.04 mg of unlabelled diphenyl. A Rinco evaporator was used to remove the benzene; 95.8% of the radioactivity was found in the flask and 1.6% was found in the trap to the vacuum line. The specific activity of the carrier diluted radiotracer was determined by liquid scintillation counting to be 2.68×10^4 dpm/µg.

An acetone solution (100 ml) containing 218.7 μg of diphenyl-^{14}C per ml was prepared from the diluted radiotracer. Another dilution with acetone was made to obtain a ^{14}C-diphenyl concentration of 4.66 μg/ml.

Fish Exposure and Clearance by J. S. Brosier of Waste Control

A continuously metering, diluter system was used by Sam Brosier of Waste Control to maintain the concentration of ^{14}C-diphenyl in the exposure tanks. A liter of the acetone solution of ^{14}C-diphenyl (4.66 μg/ml) was added to the metering reservoir.

A thousand-fold water dilution by the diluter gave an exposure level of 10 ppb in the first exposure tank. A subsequent 10-fold dilution gave an exposure level of 1 ppb in the second exposure tank. Thus exposure levels of 10 ppb and 1 ppb could be maintained simultaneously. This equipment is described in the report on ^{14}C-diphenyloxide.

Forty fish were exposed at 1 ppb, another 40 at 10 ppb, and 4 were kept as unexposed controls. Four fish were removed from each tank at 6 hr, 12 hr, 24 hr, 48 hr, 96 hr. Water was also sampled at these times.

The fish were filleted and separated into flesh and remainders, and frozen until they could be radioassayed. The water was sampled by pipetting 5 ml aliquots directly into 15 ml of Bray's scintillator. These counting samples were stored in a refrigerator until radioassayed.

After 96 hr of exposure, the fish were cleared in continuously changing fresh water. At clearing times of 6 hr, 12 hr, 24 hr, 48 hr, and 96 hr, 4 fish were removed from each tank. The clearance water was not sampled.

Radioassay of the Water

The ^{14}C-diphenyl was determined by direct counting of the 5 ml water aliquots by liquid scintillation counting in a Packard TriCarb 3324 liquid scintillation spectrometer.

Radioassay of the Fish

All fish flesh and remainders were homogenized in a Virtus grinder. All the fish samples except the uptake flesh samples were combusted in a Harvey Oxidizer. Duplicate aliquots of 100 to 200 mg were combusted. The $^{14}CO_2$ formed was trapped in an ethanolamine/2-methoxyethanol (70/30) solution, mixed with a premixed toluene-xylene liquid scintaillation fluor (Econo flor), and counted in a Packard Tri-Carb liquid scintillation spectrometer, model 3380. The uniformity in quenching of the samples allowed us to correct for the quenching by a representative standards technique. The combustion efficiency was obtained by directly counting and combusting aliquots of a standard solution of diphenyl-C^{14} in acetone-water. An average combustion efficiency of 78.5% was found for the diphenyl. The µg of diphenyl-^{14}C in the fish were calculated from the radioactivity found and the specific activity of the diphenyl-^{14}C.

The uptake flesh samples (100 to 200 mg) were solubilized in 2 ml of Soluene-100 by shaking the samples overnight at room temperature. The solubilized samples were mixed with toluene-ethanol liquid scintillation counting fluid and counted with a Packard Tri-Carb liquid scintillation spectrometer model 3380. An external source channels ratio method was used to correct for quenching in the samples. The µg of ^{14}C-diphenyl was calculated from its sp. activity.

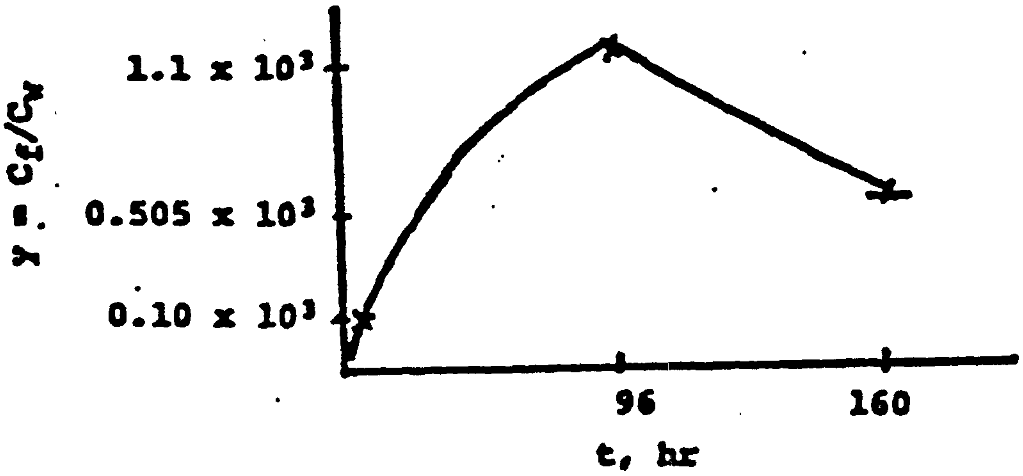
The ppm diphenyl-^{14}C in whole fish was calculated from the weights of flesh and remainders, and their respective radioassays.

RESULTS

All analytical data on fish and water are tabulated in Table 1, 2, 3, and 4. The uptake and clearance data at 1 ppb exposure is plotted in Figure 1. The data at 10 ppb exposure are plotted in Figure 2. The composite uptake and clearance profile for diphenyl is plotted in Figure 3. The diphenyl concentration in the water, C_w, is the accumulated exposure level at any given uptake time and was calculated from the actual concentration found.

From the data in Figure 3, the clearance half-life for diphenyl, $t_{1/2}$, equals 64 hr. The bioconcentration factor, BCF, equals 1900. The model appears to be a one compartment model. The calculations are on the following page.

AUTHORS Irene T. Tofalsch[?] Frank A. Blinn[?]



Clearance $t_{1/2} = 160-96 = 64$ hr

$$k_2 = .693/64 = 0.0108 \text{ hr}^{-1}$$

$$\frac{dc_f}{dt} = k_1 C_w - k_2 C_f$$

$$k_1 = \frac{1}{C_w} \frac{dC_f}{dt} + k_2 \frac{C_f}{C_w}$$

Let $C_f/C_w = y$

$$dC_f = C_w dy$$

$$k_1 = \frac{dy}{dt} + k_2 y$$

$$k_1 = \frac{(0.10-.00)10^3}{5} + 0.0108(0.10)(10^3) = (0.021)10^3 \text{ hr}^{-1}$$

$$BCF = k_1/k_2 = \frac{.021(10^3)}{0.0108} = 1900$$

$$\boxed{\begin{aligned} k_1 &= 21 \text{ hr}^{-1} \\ k_2 &= 0.0108 \text{ hr}^{-1} \\ BCF &= 1900 \end{aligned}}$$

Note: The approximation here is that the tangent to the curve at the first data point is coincident with the straight line from the origin to that point.

TABL

UPTAKE OF DIPHENYL-^{14}C IN FISH AT 1 PPB EXPOSURE

Water Analysis			Fish	Fish Analysis										
Time	C_w,	ppb	No.	W_f	C_f,	ppm		W_R	C_R,	ppm		W_t	C_t,	ppm
0	0.95		109	5.03 g	.024			4.98 g				10.01 g		
	0.93	0.94			.034	.029								
			110	5.15	.013			5.23				10.38		
					.044	.028								
			111	6.58	.019			7.54	.013			14.12		
					.025	.022			.001	.007				
			112	9.33	.011			9.57	.002			18.90		
					.025	.018	.024		.002	.002	.004			
6 hr	0.38		113	7.66	.024			8.12	.085			15.78		
	0.34	.036			.017	.021			.077	.081			0.052	
			114	4.76	.038			6.16	.107			10.92		
					.071				.112	.110			0.088	
					.045									
					.086	.060								
			115	6.43	.014			6.54	.069			12.97		
					.010	.012			.111	.090			0.051	
			116	9.25	.005			9.08	.072			18.33		
					.001	.003	.039		.078	.075	.085		0.064	.064
12 hr	0.35		121	9.19	.058			10.51	.202			19.70		
	0.35	0.35			.027	.043			.194	.198			0.126	
			122	4.19	.055			4.96	.200			9.15		
					.058	.057			.190	.195			0.132	
			123	3.46	.094			4.32	.209			7.78		
					.034				.210	.210			0.142	
					.047									
					.052	.057								
			124	5.92	.070			7.66	.211			13.58		
					.046	.058	.054		.185	.148	.200		0.136	0.134
24 hr	0.49		129	13.62	.100			14.42	.414			28.04		
	0.49	0.49			.078	.089			.385	.400			0.249	
			130	6.7	.040			7.11	.338			13.81		
					.051	.046			.346	.342			0.198	
			131	7.86	.049			8.15	.334			16.01		
					.044	.047			.332	.333			0.193	
			132	6.3	.045			6.82	.404			13.12		
					.065	.055	.060		.404	.424	.370		0.210	0.213

AR100046

TABLE 1 CONTINUED

UPTAKE OF DIPHENYL-^{14}C IN FISH AT 1 PPB EXPOSURE

Water Analysis			Fish	Fish Analysis										
Time	C_W	ppb	No.	W_f	C_f,	ppm		W_R	C_R,	ppm		Wt	C_t,	ppm
48 hr	0.62		137	8.24	.169			8.86	.806			17.10		
	0.58	0.60			.127	.148			.910	.858			0.516	
			138	7.36	.102			6.89	.821			14.25		
					.214				.752	.786			0.472	
					.158									
					.228	.178								
			139	6.62	.029	(omit)		7.77	.640			14.39	0.464	
					.329				.689	.664				
					.142									
					.217	.229								
			140	2.25	.074			3.3	.560			5.55		
					.060	.067	.156		.549	.555	.716		0.489	0.485
96 hr	0.61		145	12.4	.145			12.55	1.26			24.95		
	0.64	0.63			.147	.146			1.23	1.25			0.701	
			146	5.77	.148			5.7	0.757			11.47		
					.125	.137			0.810	0.783			0.458	
			147	3.52	.273			4.62	0.996			8.14		
					.313	.293			1.050	1.023			0.707	
			148	4.03	.162			4.97	1.23			9.00		
					.168	.165	.185		1.08	1.15	1.05		0.663	0.632

AR100047

... FISH AT 1 PPB EXPOSURE

Water Analysis			Fish Analysis										
Time	C_w, ppb	Fish No.	W_f	C_f	ppm		W_R	C_R,	ppm		Wt	C_t,	ppm
6 hr (102)		153	4.04	.222			5.53	.804			9.57		
				.223	.222			.887	.846			0.583	
		154	7.7	.179			8.34	.689			16.04		
				.185	.182			.700	0.695			0.449	
		155	8.09	.183			9.12	.941			17.21		
				.171	.177			1.013	0.977			0.601	
		156	7.63	.113			7.82	0.595			15.45		
				.115	.114	.174		0.632	.614	.783		0.482	0.529
12 hr (108)		161	6.71	.145			6.89	0.754			13.60		
				.136	.141			0.734	.744			0.446	
		162	7.58	.103			8.99	0.572			16.57		
				.096	.100			0.519	.546			0.342	
		163	6.7	.146			7.78	0.842			14.48		
				.153	.150			0.854	.848			0.525	
		164	4.7	.104			5.13	0.872			9.83		
				.098	.101	.123		0.931	.902	.760		0.455	0.442
24 hr (120)		169	5.85	.215			6.83	10.24			12.68		
				.255	.235			0.870	0.947			0.619	
		170	9.41	.128			8.85	0.766			18.26		
				.129	.129			0.818	0.792			0.450	
		171	10.29	.150			9.94	0.809			20.23		
				.160	.155			0.794	0.802			0.473	
		172	9.94	.163			10.79	0.933			20.73		
				.178	.171	.173		0.991	0.962	.876		0.539	0.520
48 hr (144)		177	8.78	.106			9.78	0.453			18.56		
				.184	.145			0.417	0.435			0.298	
		178	4.57	.078			5.84	0.413			10.41		
				.081	.080			0.384	0.399			0.259	
		179	6.28	.179			7.32	0.635			13.60		
				.152	.166			0.766	0.701			0.454	
		180	6.12	.057			6.83	0.356			12.95		
				.059	.058	.112		0.367	0.362	0.475		0.218	0.307
6 hr 192)		185	14.64	.050			13.87	.411			28.51		
				.046	.048			.432	.422			0.205	
		186	10.21	.117			10.23	.662			20.44		
				.111	.114			.656	.659			0.330	
		187	6.66	.037			7.39	.279			14.05		
				.040	.039			.283	.290			0.1[illegible]	
		188	3.44	.028			[illegible].39	.131			7.83		
				.019	.024	.056		.146	.139	[illegible]		[illegible]	

TABLE 3

UPTAKE OF DIPHENYL-^{14}C IN FISH AT 10 PPB IN WATER

Water Analysis			Fish	Fish Analysis										
Time	C_W, ppb		No.	W_f	C_f, ppm			W_R	C_R, ppm			Wt	C_t, ppm	
0	10.15		109	5.03 g	.024			4.98 g				10.01		
	10.17	10.16			.034	.029								
			110	5.15	.013			5.23				10.38		
					.044	.028								
			111	6.58	.019			7.54	.013			14.12		
					.025	.022			.001	.007				
			112	9.33	.011			9.57	.002			18.90		
					.025	.018	.024		.002	.002	.004			
6 hr	3.15		117	14.45	.290			15.14	1.16			29.59		
	3.07	3.11			.255	.273			1.24	1.20			0.614	
			118	5.39	.272			7.31	0.93			12.70		
					.315	.294			0.95	0.94			0.666	
			119	8.47	.189			8.25	0.97			16.72		
					.232	.211			0.94	0.96			0.581	
			120	7.72	.333			7.76	0.70			15.48		
					.235	.284	.265		0.68	0.69	.95		0.608	.617
2 hr	3.50		125	10.07	.459			10.78	1.40			20.85		
	3.59	3.55			.443	.451			1.56	1.48			0.983	
			126	11.55	.541			12.37	1.90			23.92		
					.644	.593			1.92	1.91			1.274	
			127	8.49	.388			8.23	1.98			16.72		
					.382	.385			1.73					
									1.50	1.74			1.052	
			128	9.51	.645			9.64	2.15			19.15		
					.652	.649	.519		2.01	2.08	1.80		1.164	1.118
1 hr	4.10		133	8.22	.503			7.9	3.47			16.12		
	4.16	4.13			.523	.513			3.46	3.47			1.701	
			134	11.62	1.008			12.57	4.22			24.19		
					.941	.975			3.76	3.94			2.073	
			135	6.2	.903			7.83	3.81			14.03		
					.757	.830			3.90	3.85			2.149	
			136	5.4	.904			5.75	4.11			11.15		
					.894	.899	.804		4.30	4.20	3.88		2.390	2.078

TABLE 3 CONTINUED

UPTAKE OF DIPHENYL-^{14}C IN FISH AT 10 PPB IN WATER

Water Analysis			Fish	Fish Analysis										
Time	C_w, ppb		No.	W_f	C_f, ppm			W_R	C_R, ppm			W_t	C_t, ppm	
48 hr	5.37		141	10.37	2.129			10.92	9.96			21.29		
	5.48	5.43			2.199	2.164			9.05	9.51			5.932	
			142	5.53	1.024			6.67	6.35			12.20		
					1.171	1.098			6.59	6.47			3.537	
			143	7.42	1.495			7.93	6.87			15.35		
					1.915	1.705			6.95	6.91			4.394	
			144	4.77	1.954			5.65	9.71			10.42		
					2.390	2.172	1.785		8.19	8.95	7.96		5.847	4.928
96 hr	6.38		149	7.74	1.153			7.03	9.39			14.79		
	6.24	6.31			1.651	1.402			9.64	9.51			4.526	
			150	9.71	3.040			9.82	16.08			19.53		
					3.115				15.67					
					2.77				15.66					
					3.39				12.89	15.08±.73				
					3.32									
					3.22	3.14							7.582	
			151	10.67	1.832			10.89	12.84			21.56		
					2.595				12.91					
					1.89				13.65					
					2.65				13.16	13.14±.18				
					2.63									
					2.58	2.363							6.637	
			152	4.5	0.730			4.91	6.36			9.41		
					0.646	0.688	1.898		6.25	6.31	11.01		3.292	5.509

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TABLE 4

CLEARANCE OF DIPHENYL-^{14}C FROM FISH AT 10 PPB EXPOSURE

Water Analysis		Fish	Fish Analysis									
Time	C_w, ppb	No.	W_f	C_f, ppm			W_R	C_R, ppm			W_t	C_t, ppm	
6 hr (102)		157	7.12	1.92			7.93	11.00			15.05		
				1.96	1.94			10.86	10.93			6.68	
		158	5.81	3.46			6.78	11.85			12.59		
				3.42	3.44			12.38	12.12			8.11	
		159	5.22	2.08			6.31	10.82			11.53		
				1.81	1.95			11.42	11.12			6.09	
		160	3.6	0.85			4.17	3.43			7.77		
				0.73	0.79	2.03		3.18	3.30	9.37		2.14	5.76
12 hr (108)		165	10.02	1.62			11.44	6.96			21.46		
				1.68	1.65			7.01	6.99			4.48	
		166	4.38	1.70			5.17	6.23			9.55		
				3.28	2.49			6.07	6.35			4.58	
		167	7.31	1.94			8.85	9.08			16.16		
				1.83	1.89			7.72	8.40			4.60	
		168	7.36	2.66			8.76	12.76			16.12		
				2.72	2.69	2.18		14.29	13.53	8.83		4.80	4.61
24 hr (120)		173	5.42	1.36			6.45	5.82			11.87		
				1.36	1.36			5.75	5.78			3.14	
		174	10.83	1.05			10.45	5.69			21.28		
				1.40	1.22			6.21	5.95			2.87	
		175	5.84	1.67			6.74	9.56			12.58		
				1.80	1.74			10.85	10.21			5.47	
		176	7.53	2.23			7.5	12.69			15.03		
				2.07	2.15	1.62		12.25	12.47	8.60		6.22	4.43
48 hr (144)		181	9.15	1.07			8.86	10.80			18.01		
				1.01	1.04			9.22	10.01			4.92	
		182	5.56	1.23			6.87	7.91			13.43		
				1.19	1.21			8.22	8.07			4.13	
		183	11.63	1.29			10.92	8.29			22.55		
				1.59	1.44			8.31	8.30			4.02	
		184	5.76	0.92			6.91	6.23			12.67		
				0.98	0.95	1.15		6.47	6.35	8.18		4.99	4.52
96 hr (192)		189	8.54	0.22			8.9	2.46			17.44		
				0.18	0.20			2.48	2.47			1.36	
		190	5.94	0.37			6.86	3.63			12.80		
				0.37	0.37			3.26	3.45			[illegible]	
		191	7.94	0.48			9.12	1.85			17.06		
				0.43	0.45			1.83	1.84				

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LOCATION	DEPARTMENT	DATE
MIDLAND, MICHIGAN	Chemical Biology Research	Dec. 10, 1971

AUTHOR: W. B. Neely

TITLE: DOWTHERM® A and the Environment

D-1041

INFORMATIVE SUMMARY WITH CONCLUSIONS

REVIEWED BY

Based on the known properties of DOWTHERM A and its use pattern, an analysis of the potential impact of this heat exchange fluid on the environment was made. The results would indicate that its present use will tolerate a slow leak (25 lbs/day) into a stream which has a minimum flow rate of approximately 200 cubic feet/second. Fail safe conditions should be installed at the site to prevent accidental spills of large quantities into the stream.

Characteristics of this product including biodegradability and a sufficiently low partition coefficient to preclude bioaccumulation suggest that it is a safe ecological material when used appropriately. The ecological hazard that may be incurred with DOWTHERM A appears to be much smaller than that incurred with polychlorinated biphenyls. In view of these findings and a demand for a replacement for the PCBs we recommend that the following work be undertaken.

1. Establish the movement of this material in the environment experimentally.
2. Study the metabolism and accumulation pattern of DOWTHERM A. in aquatic speices and compare it with PCB.

Further recommendations are made in the report.

MIDLAND 22-1053

ISSUED TO

DEPARTMENT	ATTENTION OF	DEPARTMENT	ATTENTION OF

JUN 20 1984

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DOWTHERM A AND THE ENVIRONMENT

INTRODUCTION

DOWTHERM® A, a eutectic mixture of diphenyl (DP) and diphenyl oxide (DPO), is an industrial heat transfer agent. Cu rently, there is considerable pressure to discontinue the use the principal competitor, the polychlorinated biphenyls (PCBs Because the use of PCBs is under fire[1] questions concerning t environmental hazards that may be incurred with the use o D THERM A are being asked. The purposes of this report are as follows: 1. to develop a model which may aid in integrating data and predicting the environmental hazard, 2. to summariz the available data relevant to answering these questions, and 3. to suggest additional studies which are needed to support continued use of DOWTHERM A.

I. THE ENVIRONMENTAL QUESTIONS

The questions were of two types: 1) what is the effect of a shock load on a river? This may occur when several thousand gallons are accidentally dumped into a river, 2) the second question concerns the environmental impact of a slow leak into a river.

In analyzing the slow leak problem further, the following picture emerges.[2] A typical system uses 90,000 pounds. The loss from such a system as indicated by the make up sold to a customer amounts to 9,000 pounds/year. Assuming that all is lost to a river, 25 lbs/day would enter the river.

For a river flow of 300 cubic feet/second (minimum flow of Tittabawassee) to 800 cubic feet/second the following calculations can be made:

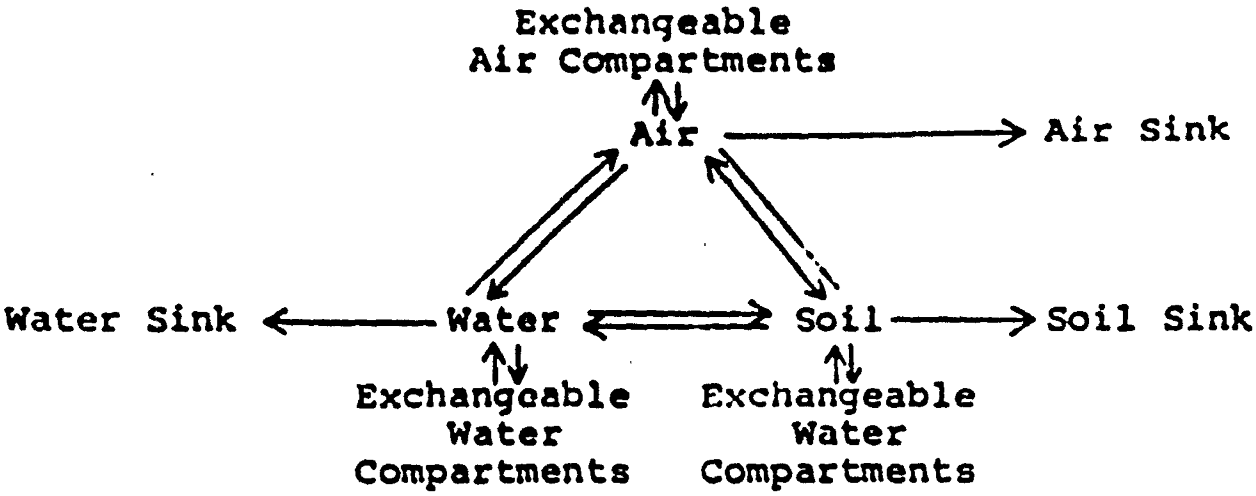
300 cu ft/sec = 200 $\bar{M}$ gallons/day = 1660 $\bar{M}$ lbs/day
This flow will dilute 25 lbs to 0.015 ppm by weight.

800 cu ft/sec will dilute 25 lbs to 0.0062 ppm by weight.

Obviously, the magnitude of any chronic problem will be intimately associated with the characteristics of the water system near the location.

II. THE MODEL

Once DOWTHERM A enters the stream partitioning between the three major sinks: air, water, and soil, takes place. A useful model to describe the fate of a chemical is shown in the following equation (1).



(1

In this equation, it is assumed that exchange and equilibrations of an agent occurs between three major compartments shown at the vertices of the triangle--air, water, and soil. The chemical may exit these compartments by physical or chemical deactivation. This is represented by a one-way arrow from the major compartments into a sink. Of course, it should be recognized that the single sink indicated in Equation 1 for deactivation may represent multiple methods for deactivation. The exchangeable compartments in air, water, and soil represent exchanges between different components within the major compartments. For example, exchanges between different types of soil, exchanges between particles suspended in either air or water. These exchangeable compartments may be and are very likely to be numerous.

The next section will collect together the known properties of DOWTHERM A which will be matched to this model. This will allow an evaluation of the need for additional data.

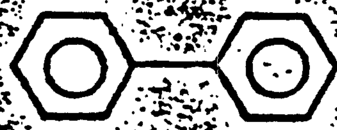
III. SUMMARY OF AVAILABLE DATA

A. Chemical and Physical Properties

DOWTHERM A is a eutectic mixture of diphenyl (26-27%) and diphenyl oxide (73-74%). The hand sheets prepared by the Thermal Laboratory provide the following information for these compounds.

TABLE I

Chemical and Physical Properties of DOWTHERM A

Parameter	Diphenyl	Diphenyloxide
Structure		
b.p.	255°	258°
m.p.	69°	27°
Density @25°C	1.156	1.07
v.p. @25°C	9.75×10^{-3} mm Hg	1.87×10^{-2} mm Hg
Solubility @25°C Water	75 ppm	21 ppm
n-Hept	112 g/100	infinite
log Partition Coef. octanol/water*	4.07	4.21
Mol wt.	1154	170

*Determined by the Analytical Laboratory.

In addition to the above, a letter[3] from W. E. Wass of Waste Control Engineering to S. Putman on October 13, 1965, has some useful data. In an aeration experiment 200 cc air/min/liter of solution was passed over a 20.5 ppm of DOWTHERM A. The results indicate that 68% is removed in 1 hour and 93% is removed in 4 hours.

B. Biological Properties

1. Aquatic Organisms. The toxicity of DOWTHERM A to aquatic species was evaluated by the Bionomics Laboratory in Wareham, Mass.[4] and is summarized in Table II.

TABLE II

Toxicity of DOWTHERM A in Aquatic Species

Species	TL50 (48 hours) Conc., ppm	No Effect Conc., ppm	No Effect Exposure Hours
Trout	2.7	1.6	120
Bluegill	2.1	1.1	120
Stickleback	1.4	0.7	120
Fathead Minnows	3.2	1.8	144
Scud* (static test)	0.04	0.02	48

*Scud is an anthropod similar to Daphnia.

Berg, et al.[5] analyzed homogenized tissues of an eviserated carp for DOWTHERM A. They reported a concentration of 110 ppm. Unfortunately, the authors did not indicate the environment from which the fish were sampled, the number of carp which were included in the evaluation, or the range of concentrations found. If it is assumed that the concentration of DOWTHERM A in the water was below the TL_{50} reported in Table II than Berg's results suggest a potential magnification factor. This observation needs to be explored in greater depth.

2. Mammalian Toxicity and Metabolism. The single dose oral toxicity of DOWTHERM A is low. All rats given 6 g/kg died while none of the rats given 2 g/kg died.[6] The cummulative toxicity appears to be low because rats survived 132 daily doses of 1 g/kg or 0.5 g/kg. This suggests that the compound must be fairly rapidly excreted.

Slight to moderate changes were observed in the histological structure of the kidneys, livers, and spleens of rats given 1 g/kg/day. Similar changes were not observed in rats receiving 0.5 g/kg/day. Decreased weight gains and increased liver and kidney weights were observed in both groups.[6]

The finding that 64% of a single dose, 1 g/kg, is excreted within 4 days following administration supports the conclusion that DOWTHERM A is not markedly accumulated in the body.[7] Free phenolic compounds and phenols conjugated with glucuronide accounted for 24 and 26 percent of that excreted respectively.

It should be emphasized that neither the toxicology studies or the metabolism study can be used as definitive evidence that DP or DPO does not accumulate in fat. DDT has a low order of accumulative toxicity and approximately 70% of an administered dose is eliminated within a few days. The portion of DDT which is retained is located primarily in the fat and is excreted slowly. None of the reported metabolism studies of DOWTHERM A include a material balance evaluation. Therefore, the 30-40% which has not been accounted for in existing studies may be located in the fat or other compartments of the body. The clearance from these pools may be very slow.

3. Biological Oxygen Demand (BOD) and Carbon Oxygen Demand (COD) of DOWTHERM A.[8] In considering the environmental hazard of DOWTHERM A, it is important to determine whether it is degradable in the environment. Data supporting the degradability of DOWTHERM A in the environment are as follows: 1. The BOD for diphenyl after 5, 10, and 20 days incubation were 0.08, 2.13, and 2.33 respectively. Theoretically, the BOD for this compound would be 3.01

2. The BOD for diphenyl oxide at the same time intervals were 7.00 2.01, and 2.16 respectively. Theoretically, the BOD for diphenyl oxide would be 2.64. 3. The COD for diphenyl oxide after 10 days of incubation is 2.19 while the theoretical COD is 2.64.

The BOD values for diphenyl and diphenyl oxide and the COD value for diphenyl oxide suggest that these compounds are susceptible to oxidation (degradation) by bacteria and by dichromate. In the case of diphenyl the low value after 5 days of incubation and a subsequent high value after 10 days suggests that bacteria may be induced to more efficiently oxidize diphenyl.

4. Screening Data. Screening data indicate the DP and DPO have either no or minimal activity on a variety of plant and insect species. A saturated solution of DP or DPO inhibits the growth of some species of bacteria--*S. aureus*, *A. niger*, and *A. terreus*.

5. Other Data for Assessing the Fate of DOWTHERM A in the Environment. The following information characterizing the biodegradability of DOWTHERM A has been reported:[10]

1. Twenty-eight days after preparing a system (closed to the air) containing 10 ppm DOWTHERM A and nonsterile Kawkawlin loamy soil, 0.2% of the diphenyl and 23% of the diphenyl oxide remained. In this case, it appears that diphenyl was more susceptible to degradation. Since only 68% and 57% of the diphenyl oxide and diphenyl were recoverable immediately following mixing, it appears that these agents are tenaciously bound to components of the soil.

2. No DOWTHERM A was recovered after 66 hours of incubation from a closed system which initially contained a 1:20 dilution of aromatic acclimated sludge and 50 ppm DOWTHERM A.

3. Within 48 hours, a species of Pseudomonas isolated from the Dow phenol return sludge degraded all of the DOWTHERM A in a closed system which initially contained 100 ppm DOWTHERM A. The diphenyl oxide disappeared faster than diphenyl.

4. No significant loss of DOWTHERM A occurred in a system containing Tittabawassee river water collected above the plant

bacterial count, 1×10^4/ml, in [illegible] did not change during the incubation. However, the type of organisms changed suggesting that DOWTHERM A selectively inhibits certain bacteria. After 5 days of incubation, 20% of the diphenyl oxide and 35% diphenyl were recovered from a closed system containing nonsterile bottom sediment obtained from the Titabawassee River above the plant site and 50 ppm DOWTHERM A. The proportion of the loss which may have been caused by binding to the sediment was not determined.

The information summarized above indicates that DOWTHERM A is degradable and suggests the ability of a system to degrade DOWTHERM A may be induced. Preliminary evidence suggests that a naive inoculum may take up to a month to acclimate sufficiently to significantly degrade DOWTHERM A.[11] In addition to degradation, binding to components of soil contributes to the loss of DOWTHERM A from various systems. The steady state level of such binding has not been determined. It was found that a portion of the DOWTHERM A bound to soil can not be extracted with hexane. Whether all of the DOWTHERM A bound to soil can be removed or whether it is susceptible to bacterial attack is unknown.

Within 24 hours, DOWTHERM A disappeared from an open system containing either sterile or nonsterile water and 20 ppm DOWTHERM A. This suggests that DOWTHERM A in an aqueous environment quickly volatilizes. Therefore, it may be important to determine the UV degradation of DOWTHERM A.

IV. RESULTS AND DISCUSSION

It is impossible to obtain sufficient data to adequately define the model described earlier for any agent. However, we [illegible] examine the movement or steady state distribution of a chemical between portions of the model. For example, the distribution of the components of DOWTHERM A between water and air may be re-

Air $\rightleftarrows$ Water

The vapor pressure of diphenyl and diphenyl oxide is 9.75×10^{-3} and 1.87×10^{-2} mm Hg respectively. Therefore the concentration of these materials, in air at saturation, can be calculated from the gas equation; $n/V = P/RT$. If n/V is expressed as moles/l, P as mm Hg, and T as absolute degrees, R will be 62. For diphenyl, the concentration in saturated air at 25°C will be 5.27×10^{-7} moles/l or 0.081 µg/ml. For diphenyl oxide, the concentration will be 1.0×10^{-6} moles/l or 0.172 µg/ml.

The concentration of diphenyl and diphenyl oxide in water at saturation are 75 and 21 µg/ml. An approximate partition coefficient for diphenyl between water and air accordingly is 75/0.08 or 940. In a similar manner a value for diphenyl oxide is calculated to be 122. Hamaker[12] has recently made the same calculation for a series of pesticides. DP and DPO have values similar to dibromochloropropane and Eptam, respectively, both of which have known volatility properties.

The calculations just presented suggest that DOWTHERM A will be quite readily lost from water to air. The rate of loss will be increased by turbulence. This hypothesis is substantiated by the finding that within 24 hours all of the DOWTHERM A disappeared from a water solution contained in an open shake flask[10] and by the finding of the Waste Control Laboratory.

Available data do not allow much speculation about the distribution of DOWTHERM A between soil and water. The data do indicate that the partitioning of DOWTHERM A between soil and water favors distribution to the soil. Indeed, a portion of the DOWTHERM A may be irreversibly bound to components in the soil.

Using the available information, the effects that may be incurred with a slow leakage of DOWTHERM A into a river or a massive spill of DOWTHERM A into a river may be hypothesized. Assuming

25 lbs/day DOWTHERM A enters a river with a flow rate of 300 cfs. The concentration of DOWTHERM A would be 0.015 ppm, well below the 96 hour no effect level in fish. The concentration would be even lower than this value because partitioning as discussed above would occur. The rate of clearance from the bottom mud will depend on the microflora present. As previously indicated, the metabolism of DOWTHERM A by microflora in the mud may be induced by persistent exposure to DOWTHERM A. Currently, information concerning the fate of DOWTHERM A lost to air is unknown. In conclusion, it is not likely that a leak like that described would have marked untoward effects on the life of the stream.

Will DOWTHERM A bioconcentrate? As indicated in the data section there are suggestions that DOWTHERM A concentrates in fish; however, the reliability of the information is questionable. Even if DOWTHERM A is not metabolized, it would not be expected to biomagnify to the same degree as DDT And PCB. The partitioning data in Table III indicates that the probability of DOWTHERM A accumulating in the fat of a particular species is much smaller than the probability of DDT and PCB accumulating in fat. In addition to the partitioning factor, the ability of DOWTHERM A to be degraded is much higher than the other two materials. Both of these characteristics will decrease the tendency of diphenyl and diphenyl oxide to accumulate and be magnified in a food chain situation.

TABLE III

Comparison of Partition Data of DOWTHERM A, PCB, and DDT

	Partition Coefficient	Reference
DDT	1×10^6	13
PCB	1×10^6	14
Diphenyl	1×10^4	Det. by Anal. Lab
Diphenyl Oxide	1×10^4	Det. by Anal. Lab

With regard to a massive spill of DOWTHERM A a concentration gradient running from 100% saturation to almost nothing would be quickly set up. Undoubtedly, aquatic life exposed to concentrations above those listed in Table II would be killed or injured. The rate of dissipation will depend on all of those factors previously mentioned, flow rate of water, partitioning, degradation, etc. In such a situation there will be some death, but an irreversible change in the ecosystem should not occur. This latter statement is supported by Edwards.[16] He claims there is good indications that when aquatic organisms are killed by a large local application of insecticides there is usually a rapid repopulation.

V. CONCLUSIONS AND RECOMMENDATIONS

1. For the situation associated with a slow leak of DOWTHERM A in the range of 25 lbs/day into a stream with a minimam flow of 200 cu ft/sec there should be no adverse effect on the ecosystem.

2. Conditions that exceed these limitations should be examined carefully.

3. Accidental spills of any major chemical should not occur. It is not only bad economics, it is bad ecologically. At best the plant sites should be diked in order that such a spill can be contained and the material dissipated and degraded before allowing it to enter the stream. If such an accident does occur we can only speculate on the effect. If the spill occurs on a major river with a large flow of water the chances of any adverse effect are minimized.

4. We recommend that the predicted movement between air, water, and soil be verified experimentally. This becomes very important as the use of DOWTHERM A incr s. We estimate $7,000 for the cost of such a study.

5. The metabolic and accumulation pattern in aquatic species should be investigated and compared with the PCBs. This type of study would be best undertaken with labeled material. The accumu-

cost for an accumulation study is $10,000-12,000.

6. In view of the tendency of this material to enter the air environment a study should be initiated to investigate the rate of degradation by ultra viclet light.

7. For the case of a shock load, we will work out the mathematics to characterize the profile of the wave of concentration as it goes down the stream under different initial conditions. This should give us some idea of what shock loads different streams can stand without an adverse effect on the ecosystem.

8. Any research or other plans to produce a derivative of these compounds which is more stable chemically should be examined with a jaundiced eye as it will surely lead to much greater environmental problems.

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